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Smoke Composition to Disseminate Capsaicinoids in Atmosphere as Sensory Irritant

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ABSTRACT

Dissemination of sensory irritants in the atmosphere with the help of an evaporating mixture is adopted. Experiments were carried out to find an alternative sensory irritant which is more irritating and less toxic than the existing sensory irritating agents and originating from a natural source. Extract of red pepper, the oleoresin, is less toxic than the existing sensory irritants and is analysed for its constituents. Thermal studies of capsaicin and the composition indicate that the composition ignites at 190 °C whereas capsaicinoids boil at 214 °C. Lactose-$KClO_3$ reaction was found to release sufficient thermal energy to evaporate capsaicinoids into the atmosphere without degeneration. The compositions are both friction and impact insensitive. The dissemination of capsaicinoids into the atmosphere was confirmed using HPLC technique.

Keywords: Red pepper, oleoresin, ortho benzylidene melanonitrile, 1- chloroacetophenone, tear gas, dibenz (b, f)-1,4 oxazepine, lactose-$KClO_3$, capsaicinoids

1. INTRODUCTION

Over the past years, considerable advances have been made in the design and development of the riot control equipment. The existing sensory irritants like ortho benzylidene melanonitrile, 1-chloroacetophenone (CN) and dibenz (b,f)-1,4 oxazepine are disseminated by dissolving in a solvent and spraying or using an evaporating mixture in the grenades. CN (tear gas) is a widely used sensory irritant popular among the law enforcement forces. The most favoured riot control offensive weapon is the CN agent commonly known as tear gas. Dibenz (b,f)-1,4 oxazepine is a relatively new compound with high peripheral irritation property[1] and is much less toxic and more effective than ortho benzylidene melanonitrile[2]. Both ortho benzylidene melanonitrile and dibenz (b,f)-1,4 oxazepine agents are disseminated in the form of liquid sprays or in a powder form. The most favoured CN grenades are less effective in drug raids and hostage rescue situations. Considering the situation faced by the police and the security forces, it became essential to develop a non-lethal weapon which would be more effective and less toxic than CN. So, an effort was made to use natural sensory irritants for developing a non-lethal weapon.

Spices are used widely to induce flavour and taste to the food. Studies have shown that substances having acid amide group and carbonyl group compounds impart hot sensation[3]. The substances having compounds with thio-ether and iso-cyanate group impart sharp sensation. The hot taste/sensation of red pepper is attributed to the presence of group of compounds called capsaicinoids that contain acid amide group

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in their structures. These compounds are responsible for the sensory irritancy in human beings and animals.

The extract of dry ripe fruits of red pepper is called oleoresin (OC)[2,3]. Oleoresin contains natural oils, fats, and colouring matter along with capsaicinoids. Oleoresin liquid sprays are biodegradable, environmentally safe, and have immediate effect on subjects under their influence. Oleoresin sprays have limitation of aiming the spray on the face of the target, keeping a safe distance. To overcome this, efforts were made to develop a sensory irritating smoke composition. The saying, "A level beyond tolerance becomes irritancy to the organs" is being taken advantage of to develop sensory irritating smoke compositions.

The sensory irritant CN is disseminated using evaporating mixture in the hand grenades used for riot control. Experiments were carried out to find an alternative irritating agent in the form of red pepper extract that is more irritating and less toxic as compared to CN. Table 1 gives the toxicology data of these irritants.

Table 1. Toxicology data for 1-chloroacetophenone, oleoresin and dibenz (b,f)-1,4 oxazepine

Irritant	RD_{50} (μg/l)	LD_{50} (mg/kg)
1-Chloroacetophenone	42.75	120
Oleoresin	33.47	800
Dibenz (b,f)-1,4 oxazepine	16.08	7500

2. EXPERIMENTAL

2.1 Materials Used

Capsaicinoid group of compounds constitute six compounds, viz., capsaicin, dihydrocapsaicin, nor-capsaicin, nor-dihydrocapsaicin, homo-capsaicin, and homo-dihydrocapsaicin. *Capsicum annum* (L) and *Capsicum fruitescens* (L) are the two major species grown in the Indian subcontinent. The ripe dry fruit extract was subjected to HPLC using C-18 reverse-phase column. Figure 1 gives the bar chart of the percentage of individual capsaicinoids present in the extract and the sensory heat values of individual capsaicinoids in scoville heat units (SHU).

Methanol (HPLC grade), oleoresin 2 per cent, 20 per cent capsaicinoids content from DRDE, Gwalior, 40 per cent capsaicinoid content from KANCOR Flavours and Extracts Ltd, Kerala; Kieselguhr (silica content > 80 %) p*H* 6.5-7.5; particle size ≥ 75 μ from trade; lactose (AR grade), passing 120 BSS; and potassium chlorate (AR grade), passing 120 BSS, were used.

2.2 Methods

(a) *Composition*: Oleoresin with 2 per cent, 20 per cent, and 40 per cent capsaicinoids content were used for the development of sensory irritant smoke composition. Oleoresin was adsorbed on kieselguhr; to it lactose and potassium chlorate in a ratio of 1:1 were added and mixed for 30 min in a sigma blade mixer to get a uniform mix.

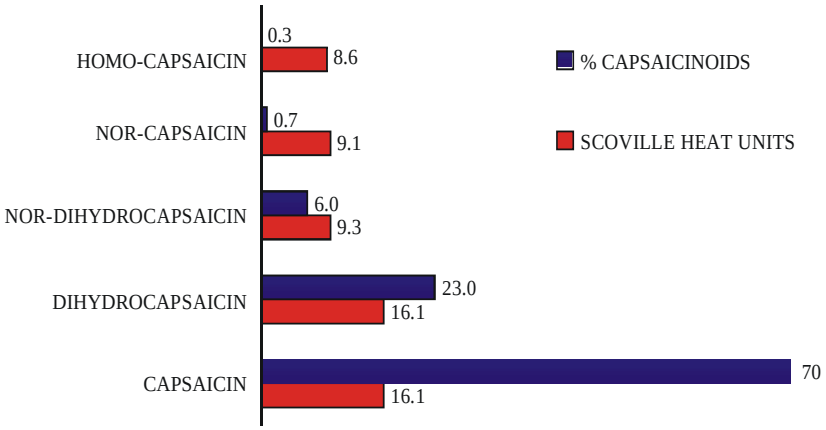

Figure 1. Distribution of capsaicinoids with scoville heat units

(b) *Burn time evaluation*: Burn time was evaluated by electrically initiating the composition pellets in an experimental pot. The compositions were pressed at 280 kg/cm^2 to get a solid pellet of 30 mm dia and 16 mm height. The smoke pot having 32 mm ID and 35 mm height was covered with a lid having four holes of 5 mm dia drilled around the central hole of 6 mm dia used for electrical ignition of the composition. Two pellets were used to measure the burn time.

(c) *Sensitivity evaluation*: Sensitivity of the composition to impact and friction was determined using Standard Bruceton Staircase method.

Impact sensitivity of the compositions was carried out using fall hammer apparatus with 2 kg drop weight and a sample mass of 20 mg. The height of 50 per cent explosion was calculated and figure of insensitivity was obtained by comparing the results obtained with standard sample composition exploding (Tetryl) (CE).

Friction sensitivity was tested using Julius Peter's friction sensitivity apparatus having a porcelain plate and pin. The composition (10 mg) was kept between the porcelain plate and pin and a weight was attached to the arm holding the porcelain pin. A two and fro motion determines whether the composition ignites or not. If the composition ignites, the next lower weight is applied and the process is repeated till no fire or ignition occurs for the five successive experiments.

(d) *Ignition temperature*: Ignition temperature was determined using indigenously fabricated DTA apparatus at 40 °C/min using 20 mg sample.

e) *Thermal studies by DTA*: Thermal studies of composition and solid capsaicin (95 % pure) were carried out using indigenously fabricated DTA apparatus. The composition was subjected to thermal studies using 20 mg composition at 20 °C/min.

f) *Smoke sampling and HPLC*: The composition was ignited electrically in a glass crucible placed in a closed glass vessel. The combustion gases of the composition liberated were dissolved in methanol and subjected to HPLC using reverse-phase C-18 column and UV detector at 210 nm. 20 l sample was injected with methanol; water was used as mobile phase, and at a flow rate of 1.2 ml/min. The HPLC run is given in Fig. 2. Standard run was carried out using pure capsaicin, Aldrich make, and pure dihydrocapsaicin, Sigma make.

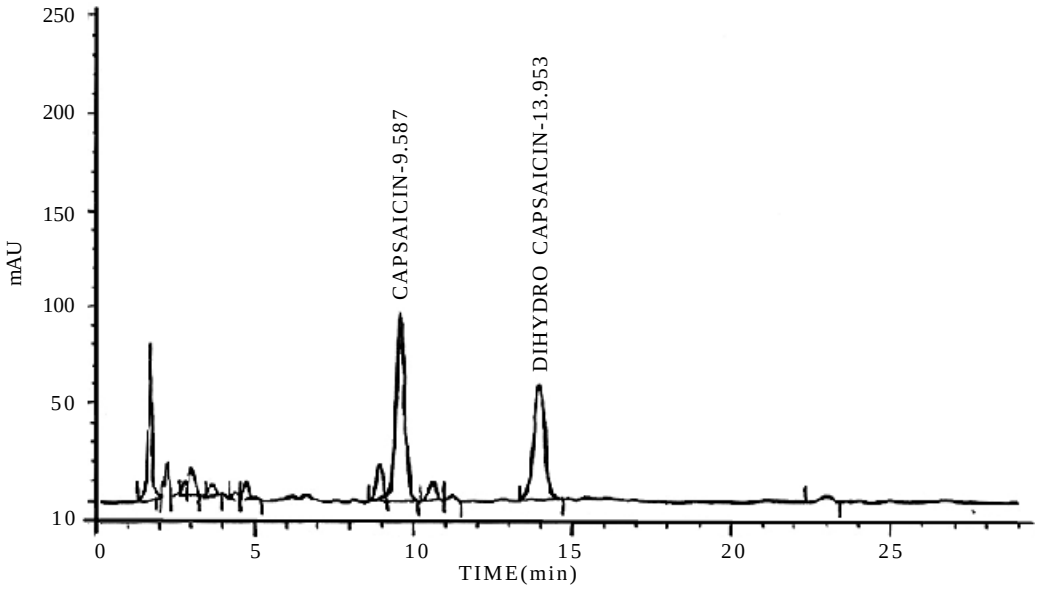

Figure 2. HPLC of smoke sample dissolved in methanol

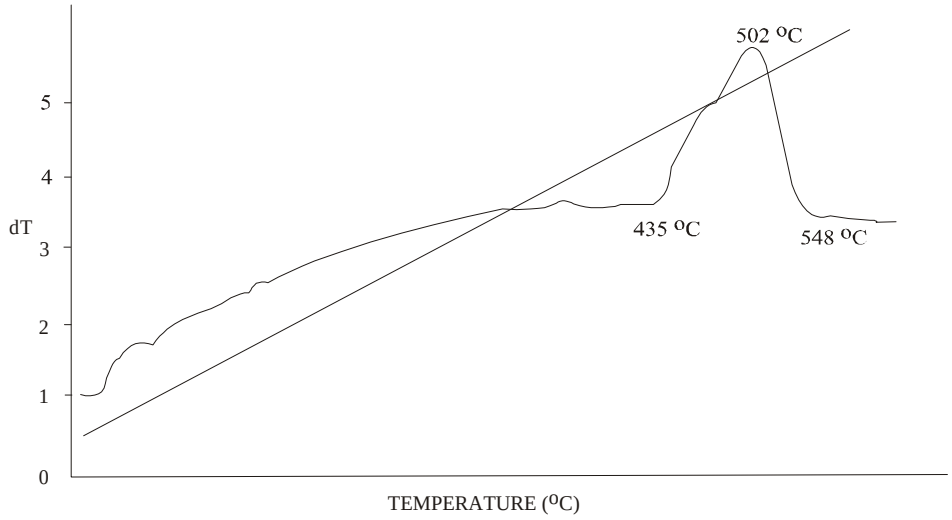

Figure 3. DTA of 95 per cent pure capsaicin

3. RESULTS & DISCUSSION

(a) *Composition*: From Fig. 1, one can see that capsaicin and di-hydrocapsaicin are the main contributors to sensory heat. Both have the sensory heat value of 16.1 SHU[4,6], followed by nor-dihydrocapsaicin-9.3 SHU, nor-capsaicin-9.1 SHU, and homo-capsaicin-8.6 SHU. Considering the percentage of individual capsaicinoids, one can say that capsaicin (70 %) and di-hydrocapsaicin (23 %) are the primary contributors to the sensory heat/irritancy while other capsaicinoids impart additional irritancy.

Compositions with 2 per cent, 20 per cent, and 40 per cent capsaicinoids-containing oleoresin were studied. When 2 per cent and 20 per cent oleoresin were used, it posed processibility problems because of the lower capsaicinoids content and higher per cent of natural oils and fats. Considering the processibility and irritants dissemination, the composition with 40 per cent oleoresin was found to be promising. The irritants delivered by these compositions were studied using HPLC technique. Composition containing 40 per cent capsaicinoids gave higher irritancy as compared to compositions with 2 per cent and 20 per cent capsaicinoids.

(b) *Burn time evaluation*: Flame occurred when the composition pellets were fired in experimental pots causing decomposition of capsaicinoids in the flame zone, thus reducing the irritancy of the smoke. When the number of holes on the lid was increased to six and hole dia to 7 mm, the flaming problem was eliminated. The burn rate was 0.67 mm/s. Various experiments were conducted with change in geometry and composition to achieve a burn rate of 0.85 mm/s to achieve desired burn time of 35 s. The pellets were tubular in geometry.

(c) *Sensitivity evaluation*: Height of 50 per cent explosion for the composition was 120 cm and height of 50 per cent explosion for CE was 82 cm at 25 °C and 45 per cent RH. The figure of insensitivity (FoI) was found to be 102. Friction sensitivity tested using Julius Peter's apparatus was found to be insensitive up to 36 kg.

(d) *Ignition temperature*: The capsaicinoids melt between 60 °C to 65 °C and exhibit boiling range between 210 °C to 214 °C. Lactose $KClO_3$ in a 1:1 ratio when subjected to DTA (heating rate 20 °C/min) was found to give the reaction peak with inception at 195 °C, peak temperature 203 °C, and final temperature 220 °C. Thus lactose-$KClO_3$ system was selected as the evaporating composition. When the smoke composition was subjected to DTA (heating rate 40 °C/min), the initiation temperature was found to be 190 °C.

(e) *Thermal studies by DTA*: Thermal studies of composition and solid capsaicin were carried out using indigenously fabricated DTA apparatus. DTA curve of solid capsaicin (95 % pure) (Fig. 3) showed a sharp peak at 502 °C with inception at 435 °C. From DTA one can say that capsaicin decomposes above 435 °C.

The DTA curves for lactose-$KClO_3$ and smoke composition are given in Fig. 4. Curve III(1) shows DTA of lactose-$KClO_3$ mixture and curve III(2) shows DTA of smoke composition. Curve III(1) shows an endothermic peak with inception at 136 °C and peak temperature at 152 °C, which is due to fusion of lactose. A sharp exothermic peak at 203 °C with inception at 195 °C is due to the reaction between lactose and $KClO_3$. An exothermic peak at 338 °C with inception at 317 °C is due to the decomposition of un-reacted lactose[7-9].

Curve III(2) shows an endothermic sink at 150 °C, which is the fusion of lactose. A sharp exothermic peak at 200 °C with inception at 195 °C is due to the reaction between lactose and $KClO_3$. The last broad peak at 505 °C with inception at 440 °C is due to decomposition of oleoresin/capsaicin trapped in kieselguhr. This matches with the decomposition temperature of solid capsaicin (95 % pure) as seen from the DTA in Fig. 3; thermogravimetric analysis indicates loss of 98 per cent of capsaicinoids at 195 °C.

(f) *Smoke Sampling and HPLC*: The standard HPLC run of capsaicin gave a sharp peak at retention time 9.9 min while di-hydrocapsaicin gave a sharp peak at retention time 14.4 min, which is in agreement with the reported values[4-6]. The HPLC run of smoke sample dissolved in HPLC grade methanol is shown in Fig. 2. HPLC run shows distinct peaks of capsaicin and di-hydrocapsaicin at retention time of 9.5 min and 13.9 min, respectively. This confirms the dissemination of active sensory irritants in the smoke.

4. CONCLUSION

Natural extract of red pepper with 40 per cent capsaicinoids content can be disseminated in the atmosphere as a sensory irritant via a smoke composition. The composition is insensitive to both impact and friction and is safe to handle. Thermal

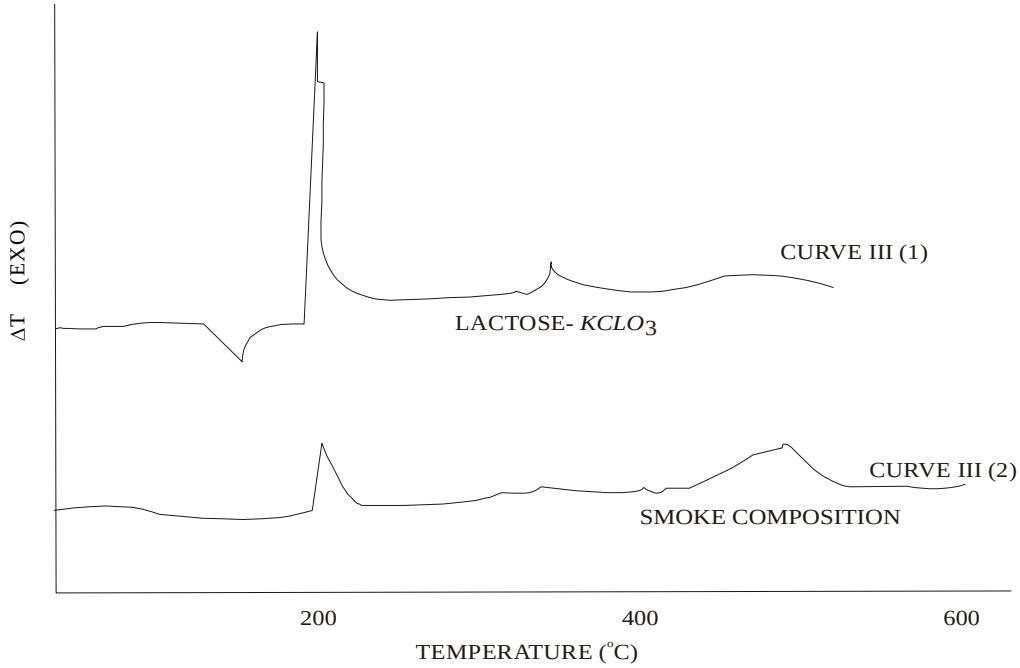

Figure 4. DTA of lactose-$KClO_3$ and smoke composition

studies indicate that the dissemination of capsaicinoids is complete without degeneration. HPLC indicates the presence of capsaicinoids in the smoke. Being a natural extract and less toxic as compared to CN agent (tear gas), it can be used in riot control, hostage-rescue situations, and for flushing out terrorists from the hideouts.

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